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Measurement of Loblolly Pine Terpene Emissions

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Research Triangle Park, NC

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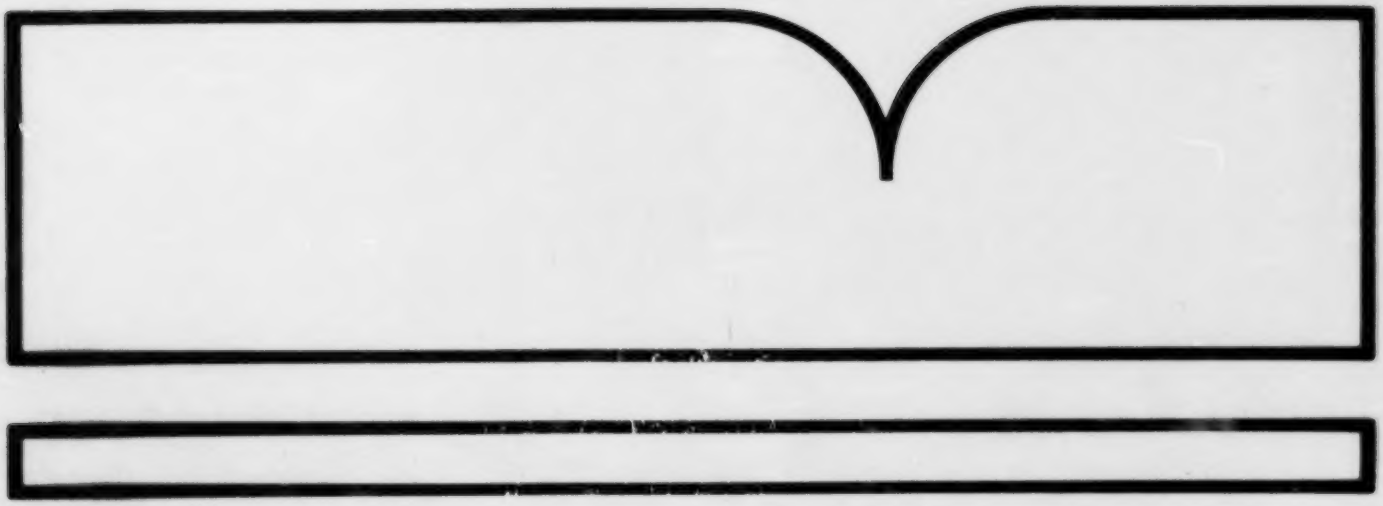

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MEASUREMENT OF LOBLOLLY PINE TERPENE EMISSIONS

by

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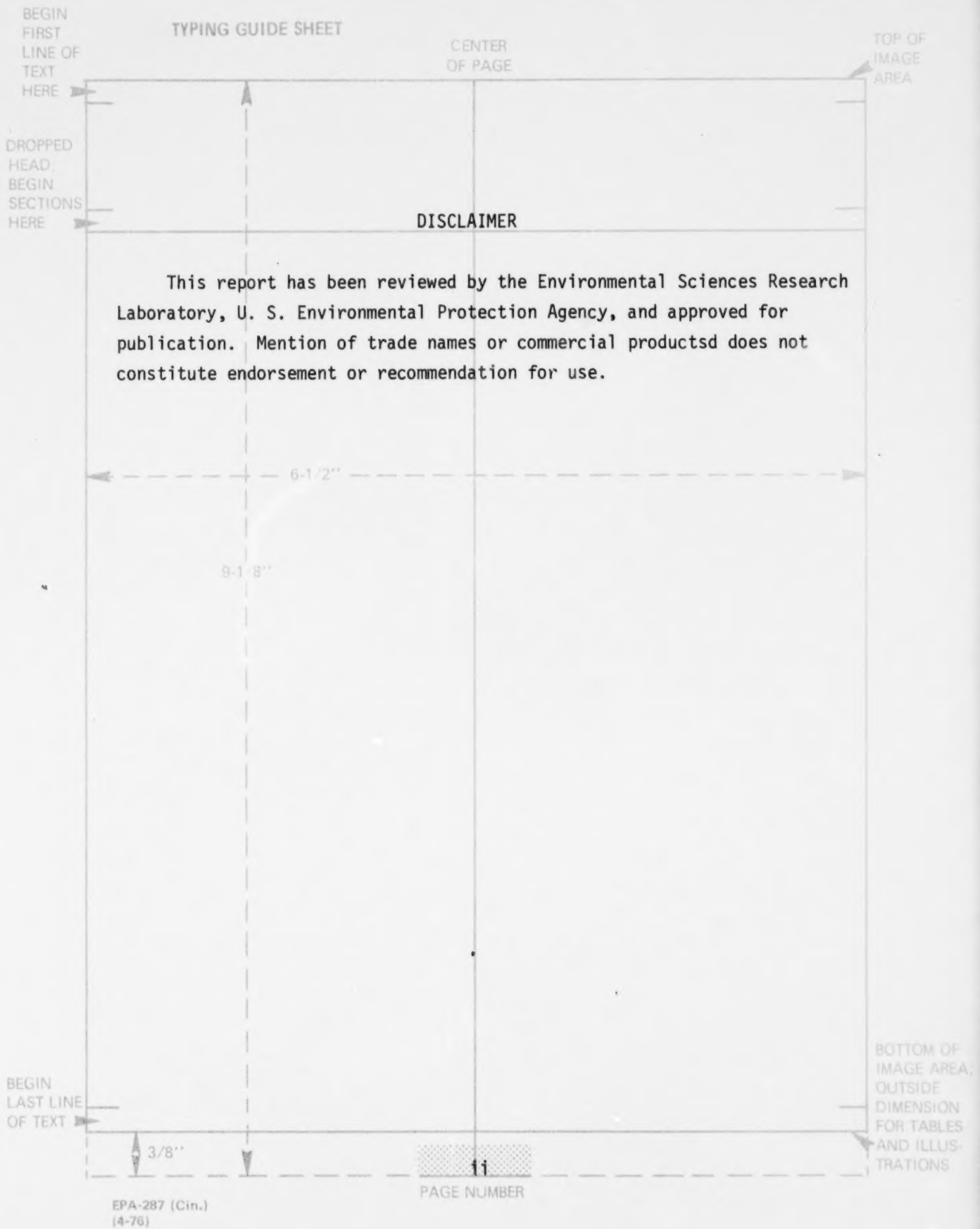

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SECTION 1

INTRODUCTION

In the mid-1960's, reports of high hourly average ozone concentrations in rural areas of the United States began to appear. Further air monitoring confirmed that ozone concentrations above the previous National Ambient Air Quality Standard of 80 ppb were not at all uncommon.[1] High rural ozone basically has three possible origins: (a) transport of ozone/precursor air from urban areas, (b) intrusion of ozone from the stratosphere, and (c) in situ photochemical generation of ozone due to the presence of biogenic organic emissions.[2] That ozone/precursor air is transported from urban areas is well documented by many studies during the 1970's.[3] However, the quantitative impact is not so well established. Singh et al.,[4] after analyzing long term ozone data collected at remote sites and aircraft data, concluded that a significant reservoir of ozone, predominantly of stratospheric origin, was present in the troposphere. However, experimental data demonstrating intrusion directly to ground level are currently lacking. The possibility that tropospheric ozone is produced by the photochemical reactions of biogenic hydrocarbons has been proposed and actively researched in recent years.[5,6] This research addresses several questions: What volatile organic compounds are emitted by vegetation? What are the emission rates and ambient air concentrations of the most abundant biogenic hydrocarbons? What is the ozone production potential of biogenic hydrocarbons? This report addresses the subject of biogenic hydrocarbon emission rates and the methodology for measuring such rates.

The earliest work determining biogenic hydrocarbon emission rates from live vegetation was reported by Went.[7] His calculations were based on unpublished data by Haagen-Smit who had "analyzed air which had passed over shrubs of Artemisia tridentata and found a release of organic

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carbon (absorbed as CO_2 after combustion) which amounted to about 50 kg per day per km^2 of vegetation."[7] The report did not detail the emission measurement methodology.

Some years later, Rasmussen identified isoprene and monoterpenes as foliar volatiles emitted from a wide variety of plants and used leaf assimilation chambers (1 liter in volume) to measure hydrocarbon emission rates of foliage on intact plants.[8]

More recently, Zimmerman developed a rapid and field-portable method to determine emission rates from live vegetation, soil-leaf litter, and water surfaces.[9] A portion of the vegetation was enclosed in a Teflon bag, an initial sample was collected, clean air was blown into the bag, and a second sample was collected. The two samples were analyzed by gas chromatography-flame ionization detection (GC-FID), and the emission rate was equal to the hydrocarbon mass gain in the enclosure bag divided by the emission time period and the foliar biomass of the enclosed vegetation. Zimmerman also described a procedure for producing an area-wide biogenic hydrocarbon emissions inventory.[9] Emission rates of representative samples of the predominant plant species were determined in the field; the biomass densities of the major species were quantified and used with algorithms that corrected for daily and seasonal variables to calculate the total emission inventory. Zimmerman used this procedure to estimate biogenic hydrocarbon inventories for the Tampa, Florida,[10] and Houston, Texas, areas.[11]

Flyckt studied the seasonal variation of volatile hydrocarbon emissions from ponderosa pine and red oak.[12] He applied Zimmerman's enclosure technique to three limbs from two ponderosa pines and one limb from one red oak. For ponderosa pine, Flyckt found a maximum of 46.9 micrograms hydrocarbon emitted per gram dry leaf mass per hour (µg/g/h) in the spring and a minimum of 1.3 µg/g/h in the fall. For red oak, the maximum was 23.5 µg/g/h in July, and the minimum was 0 from the end of September through the winter. He also found that in red oak, the ratio of isoprene emitted to carbon dioxide absorbed was a direct log-linear function of temperature. At 60°F, 0.2% of absorbed carbon was released as isoprene; this increased to 1.0% at 90°F.

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Tingey et al.[13,14] have used a slightly different and more controlled approach for measuring biogenic hydrocarbon emission rates. They used an environmentally controlled gas-exchange chamber to determine hydrocarbon emission rates for live oak and slash pine seedlings that had been preconditioned in growth chambers. Temperature and light intensity were varied to determine their effect on emission rates. The authors found that light had no direct influence on slash pine monoterpene emission rates, and that monoterpene emission rates were a log-linear function of temperature between 20 and 46°C.[14] Light and temperature both influenced the isoprene emission rate from live oak; however, the relationships did not follow a simple log-linear model.[13] Tingey et al. also developed diurnal models for monoterpene and isoprene emission rates.[13,14]

The above-mentioned methods of Rasmussen, Zimmerman, and Tingey for determining biogenic hydrocarbon emission rates are all variations of the enclosure methodology in which a plant or portion of a plant is isolated in an artificial environment. The advantages of this methodology are that it is simple to set up and use, and it is relatively inexpensive. However, there are several disadvantages. If vegetation is disturbed or damaged during sampling--which can easily happen--substantial emission rate error can occur. The final error of an emission inventory can be quite large due to the propagation of errors of its components: errors of individual species emission rate determinations, errors of vegetative density estimates, and errors due to the seasonal and diurnal correction procedures. A potentially more accurate method would be to directly measure the flux of biogenic hydrocarbons over a vegetated area and thereby reduce the propagation of errors from the estimated components.

This report presents a method for determining biogenic hydrocarbon flux over a forested area. Experimental measurements were made at a loblolly pine plantation over a six month period. Due to analytical limitations, α-pinene, which is the most abundant volatile organic emitted from loblolly pine, was the only hydrocarbon for which a flux was determined. By measuring the net radiation and vertical gradients of α-pinene, temperature, and water vapor above the forest canopy, the α-pinene flux could be calculated using an energy balance/Bowen

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ratio method.[15] This method has been used previously to measure pesticide vapor fluxes from bare soil and corn.[16] The advantages of this method are that the vegetation is not disturbed, that an area flux is determined directly, and that the emission is an integrated flux which includes all portions of the vegetation and the ground litter. This report also compares results from the energy balance/Bowen ratio approach with results from Zimmerman's enclosure method.

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SECTION 2

CONCLUSIONS

An energy balance/Bowen ratio method was used to measure biogenic emission rates of α-pinene at a loblolly pine forest. Twenty determinations of α-pinene flux were made. Values ranged from 19 to 84 $\mu g/m^2/min$, with a mean emission rate of 41 $\mu g/m^2/min$ and a mean temperature of 30^oC. Seventeen emission rate measurements were also made by a limb enclosure method. Comparison of the two techniques indicated no statistically significant difference between the two methods. However, it should be noted that both methods displayed large variances, and that the enclosure method may have yielded results biased high due to the unavoidable physical contact between the enclosure bag and the vegetation which probably caused some additional emission beyond what undisturbed vegetation would produce.

The chief advantage of the energy balance/Bowen ratio method is that a total flux, which includes emissions from leaves, ground litter, and other non-leaf vegetative surfaces, is determined directly, rather than from individual emission rates and biomass densities--both of which can have large uncertainties. The disadvantages of this method are that it is complicated and expensive and that the analytical method for the hydrocarbons must be very sensitive and specific. The advantage of the enclosure method is that it is relatively easy to perform and is field portable. The analytical requirements are not as stringent because the concentrations of biogenic hydrocarbons in the enclosure bag are much higher than ambient concentrations.

Because of the variability of the flux estimates and the lack of any simple functional relationships with environmental variables, only approximate flux estimates can be made at this time. A more complete set of emission data over the seasonal range of temperatures and a

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better understanding and description of the emission surface will probably
be required before adequate predictive emission functions can be developed.
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SECTION 3

ENERGY BALANCE/BOWEN RATIO METHOD

THEORY

The flux of α-pinene, $F_{\alpha\text{-pinene}}$, from a forest to the atmosphere can be calculated from the equation

$$F_{\alpha\text{-pinene}} = -K_{\alpha\text{-pinene}} \frac{(\alpha\text{-pinene})}{\partial z} \qquad \text{(Eq.1)}$$

where, $K_{\alpha\text{-pinene}}$ is the atmospheric turbulent diffusivity (turbulent transfer coefficient) and $\frac{(\alpha\text{-pinene})}{\partial z}$ is the vertical concentration gradient of α-pinene. By using the surface energy balance approach over the forest, α-pinene flux can be estimated without the explicit need to determine the turbulent diffusivity, $K_{\alpha\text{-pinene}}$.

This method is based on partitioning the radiant energy incident upon the forest into various components.[15,17] The balance of the radiation fluxes for a vegetated surface (all incoming minus all outgoing radiation usually called the net radiation, R_n) is utilized through the following components of energy exchange and storage:

LE = Latent heat flux--energy transported away from the surface by the vertical water vapor gradient in the form of evaporated water.

H = Sensible heat flux--energy transported away from the surface by the vertical temperature gradient.

P = Carbon dioxide flux--energy used by the trees for fixing carbon during photosynthesis minus carbon dioxide produced during respiration. The quantity measured is used to calculate net photosynthesis.

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S = Stored energy--energy absorbed by biomass, air, and water vapor that increases the temperature of the trees and the moist air inside the forest stand.

G = Soil heat flux--energy transported into soil that results in a differential raising of the soil temperature.

Thus, the surface energy balance can be expressed as

$$R_n = LE + H + P + S + G \qquad \text{(Eq.2)}$$

Previous research [18,19] has shown that H and LE are much larger than P, G, and S; therefore,

$$R_n \simeq LE + H \qquad \text{(Eq.3)}$$

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Net radiation can be measured directly. The latent energy flux term, LE, is defined by the turbulent transport of the water vapor,

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$$LE = -LK_w \frac{\partial \rho_w}{\partial z} \qquad \text{(Eq.4)}$$

where,

L = latent heat of vaporization of water,

K_w = turbulent diffusivity for water vapor, and

$\frac{\partial \rho_w}{\partial z}$ = vertical water vapor density gradient.

The sensible heat flux term, H, is defined by the expression,

$$H = -\rho_a c_p K_h \frac{\partial \theta}{\partial z}, \qquad \text{(Eq.5)}$$

where,

ρ_a = density of air,

c_p = specific heat of air,

K_h = turbulent diffusivity for heat, and

$\frac{\partial \theta}{\partial z}$ = vertical potential temperature gradient.

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By assuming that the mechanisms for atmospheric turbulent transport are the same for water vapor, heat, and α-pinene, then

$$K_w = K_h = K_{\alpha\text{-pinene}} \qquad \text{(Eq.6)}$$

Furthermore, if the quantities of water vapor, -pinene, and temperature are measured simultaneously at the same points in a vertical profile above the forest canopy, then the energy equation can be solved for the latent heat flux, LE. The energy expression is first simplified by dividing each term by the latent heat flux:

$$\frac{R_n}{LE} = \frac{LE}{LE} + \frac{H}{LE} = 1 + \beta \qquad \text{(Eq.7)}$$

hence,

$$LE = \frac{R_n}{1+\beta} \qquad \text{(Eq.8)}$$

The quantity β, the Bowen ratio, is the ratio of sensible heat flux to latent heat flux,

$$\beta = \frac{H}{LE} \qquad \text{(Eq.9)}$$

Substituting Equations 4, 5, and 6

$$\beta = \frac{\rho_a c_p}{L} \cdot \frac{\partial\theta}{\partial\rho_w} \qquad \text{(Eq.10)}$$

we arrive at,

$$LE = \frac{R_n}{1 + \frac{\rho_a c_p}{L} \cdot \frac{\partial\theta}{\partial\rho_w}} \qquad \text{(Eq.11)}$$

If we assume that the turbulent diffusivities of water and α-pinene are equal, the flux of α-pinene can be calculated from the ratio of the mass fluxes of α-pinene, $F_{\alpha\text{-pinene}}$, and water vapor, E, using Equations 1, 4, and 6. The mass flux of water vapor, E, is the latent heat flux, LE, divided by the latent heat of vaporization, L. Thus, the α-pinene flux can be calculated by

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$$F_{\alpha\text{-pinene}} = E \cdot \frac{\partial(\alpha\text{-pinene})}{\partial \rho_w} \qquad \text{(Eq. 12)}$$

EXPERIMENTAL

Study Site

The study site was a uniform 19-year-old, 3.5-hectare loblolly pine stand on a level upland bench overlooking the Haw River Bottom in east-central Alamance County, in the central Piedmont of North Carolina. The site was originally the Triangle research site of Eastern Deciduous Forest Biome of the International Biological Program (IBP).[20] As part of the IBP, the site was studied intensively by investigators from Duke University and their collaborators to develop biomass growth and energy relationship models.[21,22] A very sophisticated micrometeorological sampling and measurement system was built and used for the IBP studies. For this study, α-pinene measurement was added to this system. The site layout is shown in Figure 1.

Micrometeorological Measurement System

The micrometeorological measurement system was designed for atmospheric profile measurements of water vapor, carbon dioxide, temperature, and wind speed from ground level to a height of 25 m (10 m above the top of the canopy). Point measurements of wind direction, atmospheric pressure, and net radiation were also included. The micrometeorological measurement system can be divided into two subsystems: (1) the sampling and analysis subsystem and (2) the data aquisition and control subsystem.

The sampling and analysis subsystem consisted of two parts: the point measurements and the profile measurements. The point measurements were wind direction and net radiation. The radiation measurements were made by two Swissteco (Swissteco, Pty. Ltd., Switzerland, sold through Science Associates Inc., Princeton, New Jersey) net pyroradiometers mounted 22 m above the forest floor on a scaffolding tower (radiation tower); wind direction was measured from the top of another scaffolding tower (micrometeorological tower). The two towers were 35 m apart

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(Figure 1).

The profile measurements were temperature, wind speed, water vapor, and carbon dioxide. All of the profile measurements were made from the 25 m micrometeorological tower (Figure 2).

The wind speed measurements were performed at 11 levels using sensitive 3-cup anemometers that generated 1 electrical pulse per revolution. At each of the 11 measurement levels, 2 anemometers mounted on aluminum booms were extended perpendicularly 3 m from each corner of the southwestern side of the micrometeorological tower. Cayuga Development (Ithaca, New York) anemometers were used above the canopy.

The temperature sensors were copper-constantan thermocouple wire with 2 measurement junctions located in each of 5 gas intake ports at each measurement level, forming a 10-junction thermopile. The reference junctions were kept at $0^{o}C$ in a large ice water bath located halfway up the tower.

The gas sampling portion of the system was designed to deliver air from each of 18 levels to the water vapor and carbon dioxide analytical instruments, located in a van 80 m from the micrometeorological tower. At each level, five vertical intake ports were connected to horizontal 1.25-in (3.18 cm) polyvinyl chloride (PVC) pipe to form a sampling array which resembled the prongs on a rake. The rakes were mounted so that they could be extended out a maximum of 2 meters from the tower. The intake ports were spaced 1 meter apart to provide a horizontal spatial sample. At each level, air was drawn from the rake through a horizontal side pipe perpendicular to the rake, then through flexible tubing to a vertical vacuum manifold which extended the length of the tower. The vacuum manifold then extended on the ground from the tower 60 m to a pump. Air for analysis was subsampled from the side pipe ~2 m from the rake. The subsamples were drawn by vacuum pump from each of the 18 levels through 0.375-in (0.953 cm) polypropylene tubing to large 19-L glass mixing jars that were sequentially sampled to measure water vapor and carbon dioxide content. The mixing jars provided an averaging period of 5 min.

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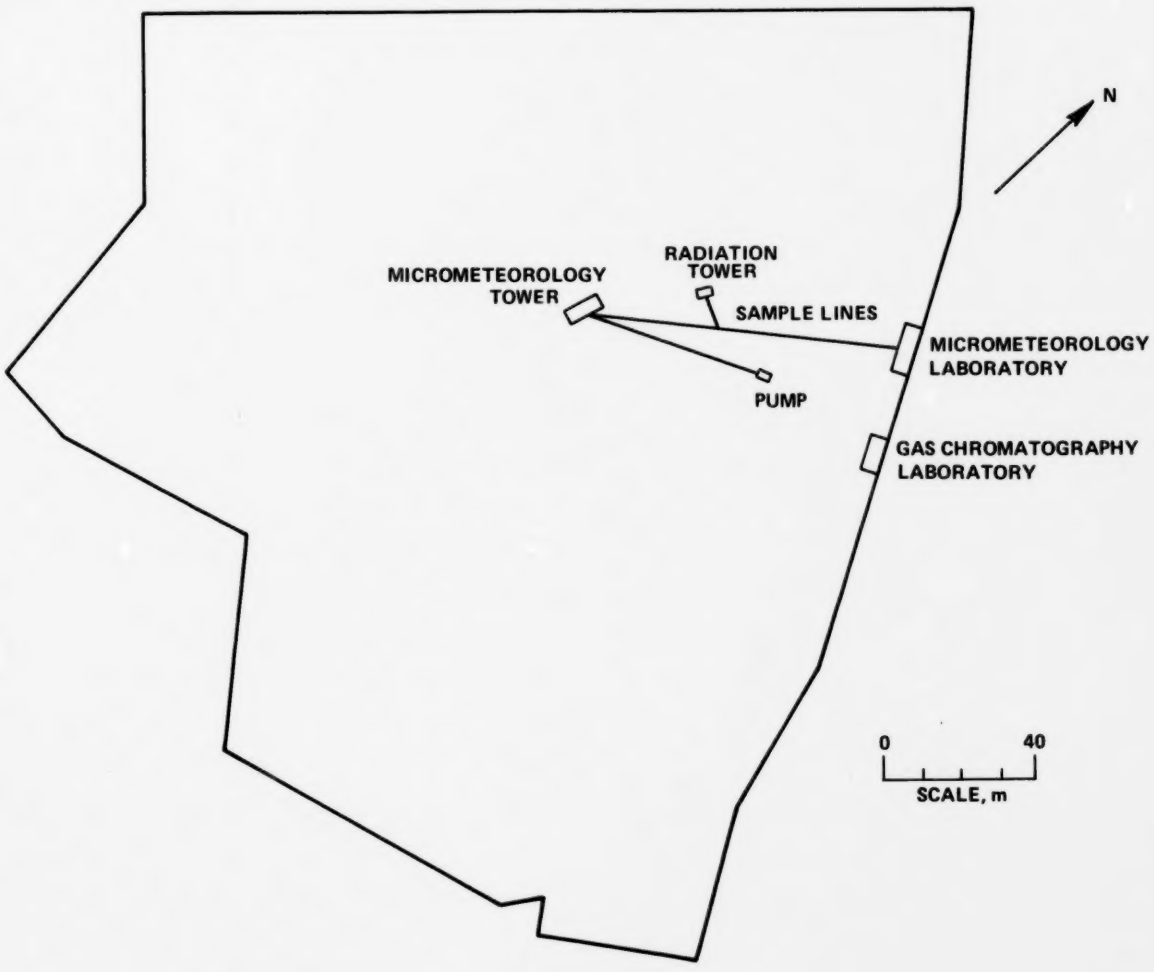

Figure 1. Loblolly pine forest research site, Saxapahaw, N. C.

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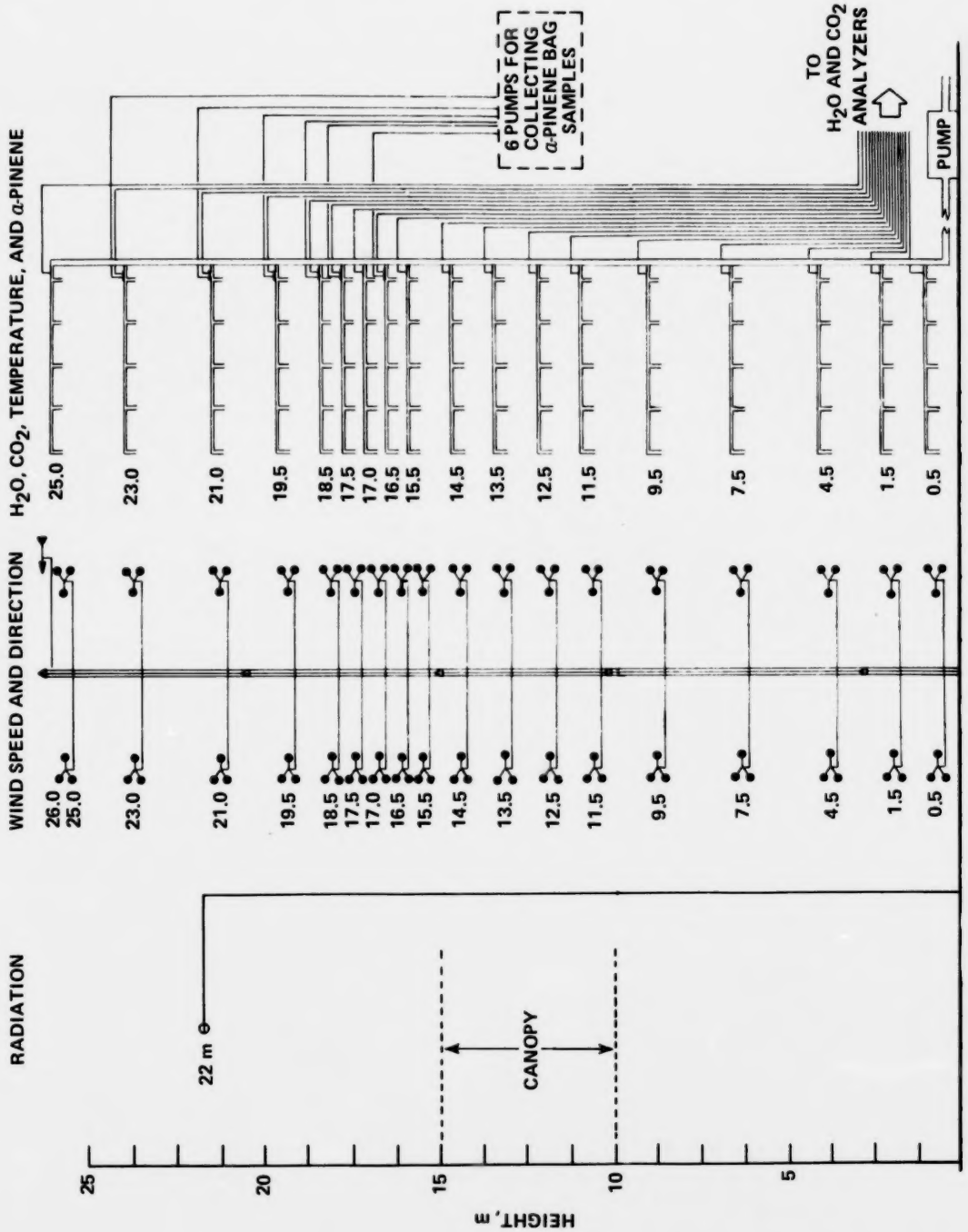

Figure 2. Micrometeorological sampling system.

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Carbon dioxide was measured by an infrared gas analyzer (IRGA), and water vapor was determined from the dew point temperature as measured by a precision dew point hygrometer. The flow of air through these analyzers was controlled by computer-directed switching of pairs of solenoid valves, so that selecting one level for measurement caused the air flow from other levels to bypass the measurement system. Each of the 18 levels was analyzed once every 5 min. Since the samples were at less than atmospheric pressure, the IRGA was calibrated, and pressure measurements were made for every sample at the dew point hygrometer and IRGA to provide corrections. Further details of the carbon dioxide/water vapor profile measurement system are explained elsewhere.[21,22]

A minicomputer controlled airflows to carbon dioxide and water vapor analyzers, performed the calibrations and pressure corrections, collected the measurements from all of the instruments, and performed calculations on the data collected.

α-Pinene Measurement System

α-Pinene measurements were made at 23.0, 21.0, 19.5, 18.5, 17.5, and 16.5 m above the forest floor (Figure 2). The air was subsampled from the micrometeorological system into Teflon bags by means of six Metal Bellows pumps (Metal Bellows Corp., Sharon, Massachusetts). The bag samples were subsequently analyzed by GC as soon as possible after collection, usually within 1 h.

Sampling of α-Pinene--

The subsampling system for one level is diagrammed in Figure 3. The same system was used for all six levels sampled. A PVC Tee was inserted into the side pipe. Inside of the PVC Tee was a 0.25-in (0.64 cm) stainless steel (SS) tube which extended 3 cm upstream of the point where the Tee was glued to the side pipe. This was to prevent sampling of adhesive solvent vapors. Teflon FEP (Polytetrafluoroethylene-hexafluoro propylene copolymer, E.I. duPont deNemours and Co., Wilmington, Delaware) 0.25-in (0.64 cm) tubing was used to transfer the sample from the Tee down to the pumps, located on a platform at the 11-m level. A bypass

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arrangement was used so that the flow rate through the Teflon lines would be high, to minimize any wall effects and at the same time provide a low flow rate into the bags, which were filled over a 30-min period. A needle valve controlled the flow rate into the bags. The bypass flow rate was 10 L/min, while the sample flow rate was 700 ml/min. The initial plumbing system did not include a needle valve between the bypass and the pump. This setup, however, did not provide good flow control into the bag at the low flow rate needed to fill the bag.

At the beginning of this study, Teflon 0.25-in (0.64 cm) polytetrafluoroethylene (TFE) tubing was run from each sampling level back to the GC lab. Later, it was discovered that the TFE tubing emitted hydrocarbons that contaminated the samples and prevented accurate sampling through long lengths of TFE tubing. Teflon 0.25-in (0.64 cm) FEP tubing was tested for contamination by GC analysis of helium blown through a 30-m length. The FEP tubing was quite clean. FEP tubing was substituted for

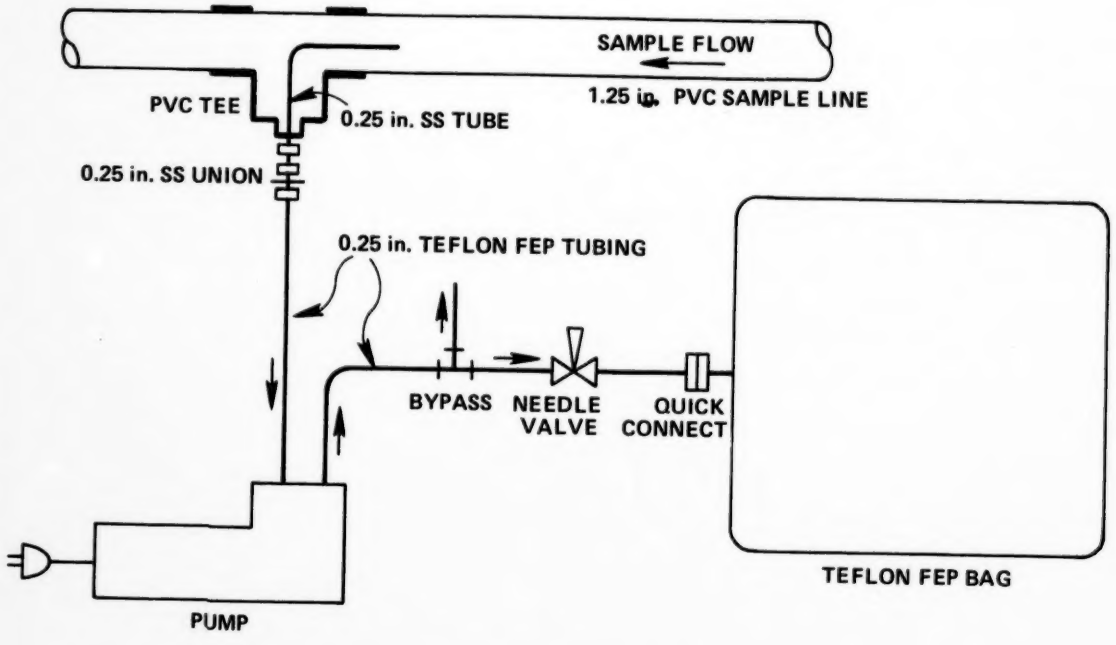

Figure 3. α-Pinene sampling subsystem.

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TFE tubing and the sample pumps were also mounted on the micrometeorological tower to make the sample lines as short as practicable.

The sample collection and storage bags were constructed of 2-mil-thick (0.05 mm) FEP Teflon film with a capacity of 25 L. Black polyethylene was used to cover the bags to protect them from exposure to sunlight. Before use, the bags were leak-checked by evacuation and visual inspection. Bags that by inspection of the chromatograms showed obvious contamination were discarded. Thirty ml of 50 ppm nitric oxide in nitrogen were added by syringe to each bag before sampling to destroy any ozone that might be present. This was done to prevent ozone reaction with α-pinene. The six samples were collected over alternating 30-min periods. This allowed a 1-h period for analysis of the six bags, thus minimizing the time that samples were stored in the bags.

Analysis of α-Pinene--

The analysis of α-pinene was performed using gas-liquid chromatography. Samples were concentrated cryogenically prior to injection, and detection was by FID. The chromatograph was a Perkin Elmer 900 with a dual valve trap/injection configuration as diagrammed in Figure 4. Liquid oxygen in a Dewar flask was the cryogen and hot water (approximately 90°C) in a Dewar flask was used to heat the trap for quick desorption of the hydrocarbons onto the column. The cryogenic trap was a 30 cm x 0.125 in (0.318 cm) o.d. SS tube filled with OV-101 on Chromosorb W(HP). Further details of the trapping injection system are discussed elsewhere.[23]

The criteria for choosing a liquid phase and column parameters were that α-pinene be separated from other hydrocarbons present in ambient air, and that the analysis time be a maximum of 15 min. Meeting these criteria proved difficult. Many pure liquid phases were tested before it was decided to test various compositions of two liquid phases mixed together. The liquid phases chosen were OV-101, a nonpolar phase, and 1,2,3-tris(2-cyanoethoxy)propane (TCEP), a polar phase. This strategy eventually proved effective.

Three mixed liquid phase columns were used during the course of the

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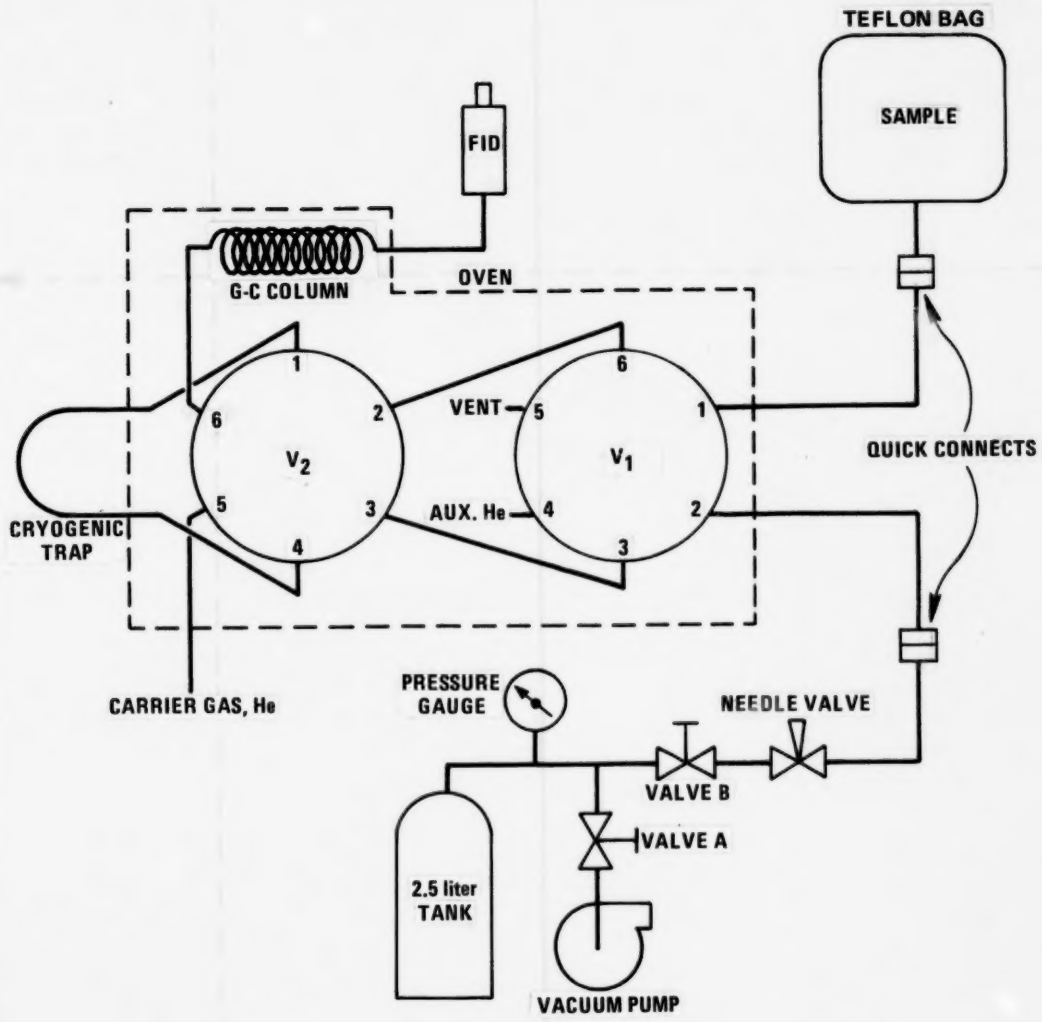

Figure 4. Hydrocarbon analysis chromatographic system.

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study. These columns and the GC analysis parameters are described in Table 1. The second GC column of Table 1 was prepared in order to shorten the analysis time from 15 min to 10 min. The third column was prepared after the second column was accidently ruined by a malfunction of the oven heater.

TABLE 1. GAS CHROMATOGRAPHY PARAMETERS FOR THE ANALYSIS OF α-PINENE

Instrument	Perkin Elmer 900 GC
Detector	Flame ionization
Carrier gas	Helium at 30 cm^3/min
Sample size	789 ml trapped cryogenically using liquid oxygen
Trap	30 cm x 0.32 cm o.d. x 0.2 cm i.d. 304 SS tubing packed with 3% OV-101 on 100/120 Chromosorb W(HP)
Columns	1. Dual columns (a and b) in series a. 1.53 m x 0.32 cm o.d. x 0.22 cm i.d. 304 SS tubing packed with 3% OV-101 on 100/120 Chromosorb W(HP) b. 1.84 m x 0.32 cm o.d. x 0.22 cm i.d. 304 SS tubing packed with a 75% OV-101, 25% TCEP liquid phase weight ratio of 3% OV-101 on 100/120 Chromosorb W(HP) and 10% TCEP on 100/120 Chromosorb P(AW) 2. Mixed liquid phase column 2.75 m x 0.32 cm o.d. x 0.22 cm i.d. 304 SS tubing packed with a 88% SP2100, 12% TCEP liquid phase weight ratio of 3% SP-2100 on 100/120 Supelcoport and 10% TCEP on 100/120 Chromosorb P(AW) 3. Mixed liquid phase column 3.1 m x 0.32 cm o.d. x 0.22 cm i.d. 304 SS tubing packed with a 90% SP-2100, 10% TCEP liquid phase weight ratio of 3% SP-2100 on 100/120 Supelcoport and 10% TCEP on 100/120 Chromosorb P(AW)

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The α-pinene peak retention time was identified by adding α-pinene to ambient air samples. The air was also drawn through mercuric sulfate/sulfuric acid olefin scrubber to test for interfering compounds. The complete removal of the α-pinene peak was good evidence of no significant interfering compounds. The peak areas were determined manually by

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calculating the height x width at half-height. Calibrations were periodically performed by analyzing α-pinene/air mixtures prepared by injecting known microliter quantities of α-pinene into Tedlar bags filled with known volumes of clean air. The replicability of the method was determined by performing duplicate analyses on 17 ambient samples. The mean percent standard deviation was ±4.2%. An accuracy of ±8.8% relative standard error was estimated by a propagation of errors of the input variables used to determine the calibration factor. These variables primarily included calibration bag flow rate measurement and microliter syringe error. A typical chromatogram of the α-pinene analysis is shown in Figure 5.

Flux Measurements--

Measurements were conducted on sunny days when westerly winds were between 1 and 5 m/s. Westerly winds were preferable since "the best fetch" was west of the tower. Because of the location of the sampling ports on the west side of the micrometeorological tower, winds from the east blew through the tower, disrupting the boundary layer from that direction. The α-pinene analyses imposed restraints on the number of data points collected, due to the time required for chromatographic analyses and sample deterioration. Three to four 30-min runs were made between 1100 and 1500 h. The runs were made at approximately solar noon when the atmosphere was in a quasi-steady state, with wind speed and direction relatively stable.

RESULTS

Table 2 lists the obtained values for α-pinene flux and the corresponding data on time, temperature, wind speed, α-pinene emission rate, and biomass density. The α-pinene fluxes were converted to emission rates for later comparison to emission rates determined by the enclosure method. This was accomplished by dividing the α-pinene fluxes by a site specific biomass density factor expressed in units of grams of dry needle biomass per square meter of land area. The biomass factor is not constant but varies with time of year. A computer simulation plot developed by Kinerson et al.[24] of foliar biomass versus time of year was used to

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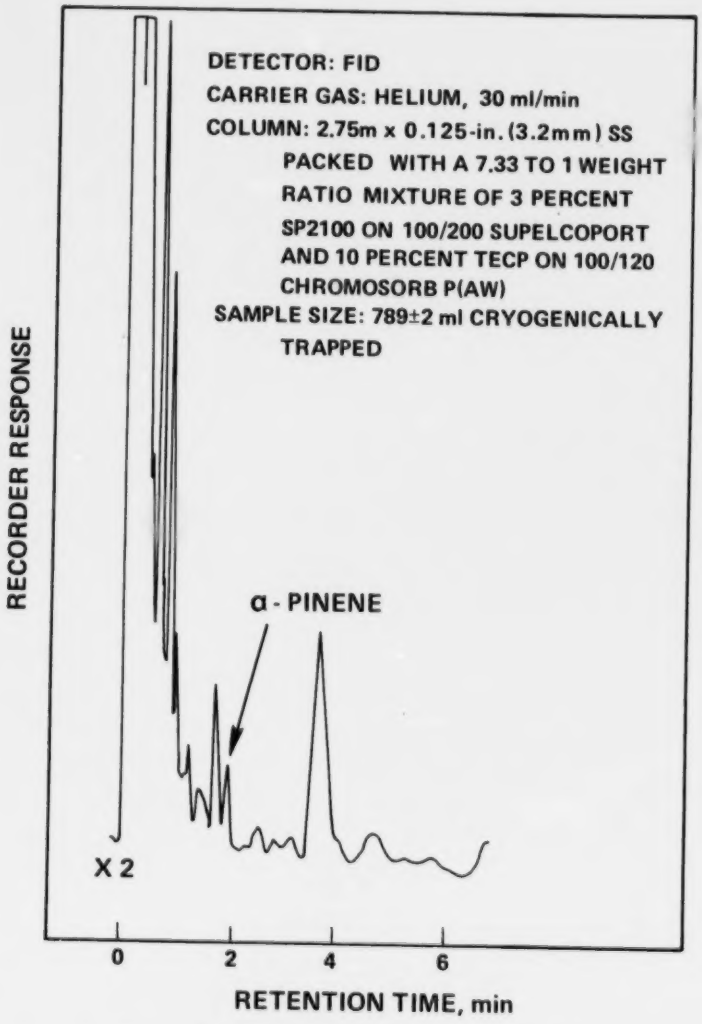

Figure 5. α-Pinene analysis chromatogram.

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determine the biomass densities in Table 2. Although the foliar biomass data was collected in 1971, the biomass data for the fall of 1971 are representative of the factors in 1977 due to the closure of the canopy during the 1971 growing season (Ralston, 1981, personal communication). A further discussion of these results and the enclosure method results follows, after presentation of the enclosure method. A typical set of profiles is illustrated in Figure 6.

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TABLE 2. SUMMARY OF FLUXES

Date 1977	Period Ending (h, EST)	Temp. (°C)	α-Pinene Flux (μg/m²/min)	R_n (W/m²)	H (W/m²)	LE (W/m²)	P (W/m²)	Wind Speed (m/s)	Biomass Factor (g/m²)	Emission Rate (μg/g/h)
7 Apr	1400	13.7	28.7	600	368	225	6	230	590	2.92
7 Apr	1430	14.9	19.2	557	339	210	9	334	590	1.95
13 Apr	1200	29.2	77.4	605	265	339	*	243	590	7.87
14 Apr	1430	28.3	47.9	626	265	351	9	345	590	4.87
30 Jun	1130	30.3	33.1	636	317	313	6	*	670	2.96
30 Jun	1230	31.1	43.5	679	374	299	6	*	670	3.90
30 Jun	1330	32.5	53.7	677	366	304	7	*	670	4.81
1 Jul	1100	29.8	43.2	684	366	335	13	*	670	3.87
1 Jul	1200	31.5	33.0	674	354	315	5	309	670	2.96
1 Jul	1300	32.3	27.7	553	270	274	10	381	670	2.48
14 Jul	1100	31.7	50.1	638	307	336	*	201	710	4.23
15 Jul	1130	31.7	83.5	691	296	388	*	204	710	7.06
18 Jul	1100	31.6	37.7	656	381	266	10	310	710	3.19
19 Jul	1130	33.4	42.2	711	373	330	9	279	710	3.57
9 Aug	1030	29.5	24.4	612	234	368	10	242	880	1.66
9 Aug	1330	33.4	24.4	718	336	378	5	226	880	1.66
10 Aug	1300	34.4	22.9	705	346	359	*	349	880	1.56
11 Aug	1130	30.2	24.4	669	95	566	8	222	880	1.66
11 Aug	1230	31.8	52.5	694	235	451	8	201	880	3.58
11 Aug	1330	32.8	59.5	664	262	399	3	221	880	4.06

* Data not available

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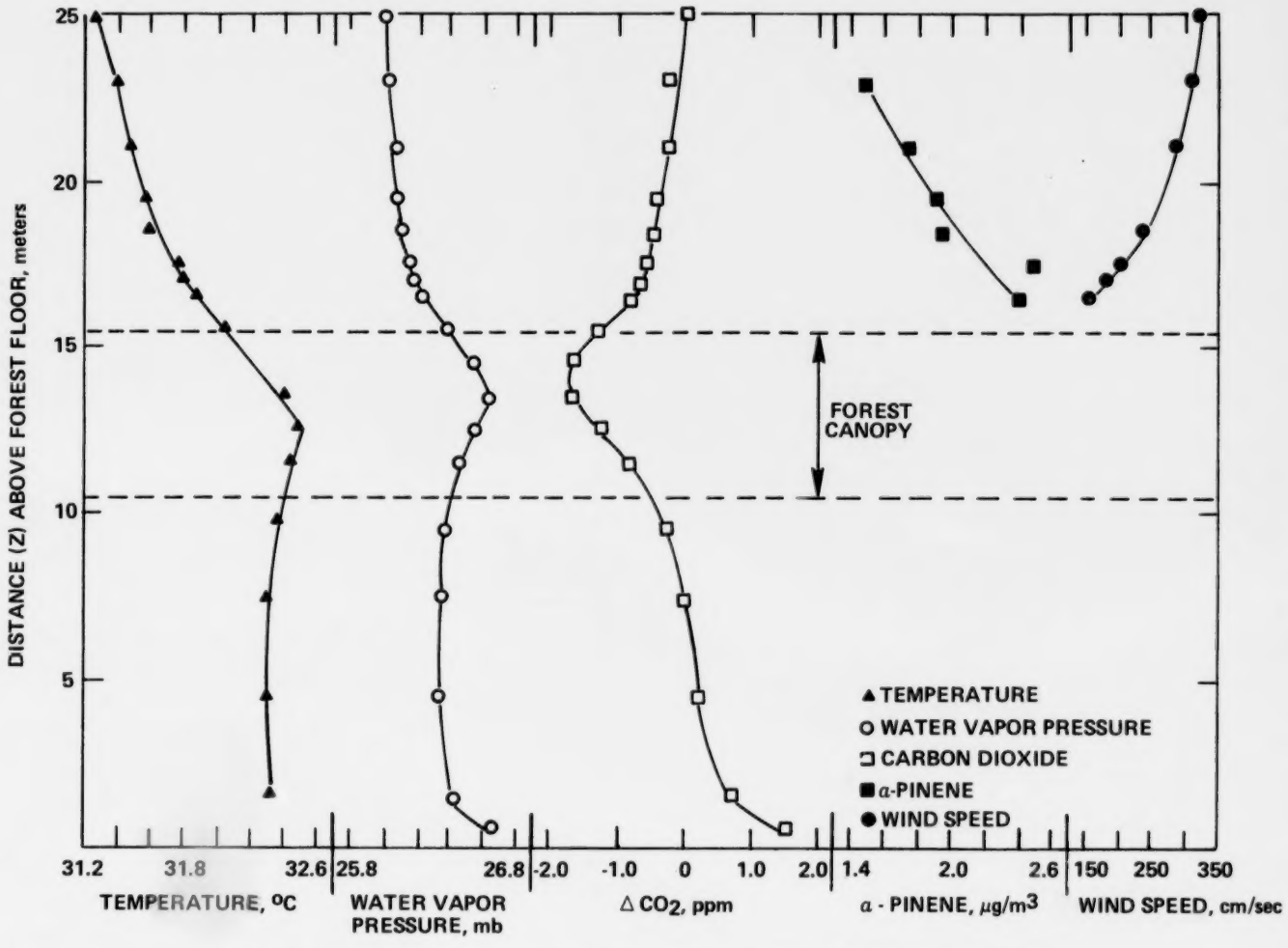

Figure 6. Loblolly pine forest vertical gradients, 7/18/77, 1035-1100 hrs EST.

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SECTION 4

ENCLOSURE METHOD

Another method for measuring emission rates from vegetation has been developed and used by Zimmerman. Zimmerman describes the method as follows:

> Basically, the method involves enclosing a portion of the vegetation of interest in a Teflon bag, sucking most of the ambient air out of the bag and thus collapsing the bag around the branch. A "background" sample of the air from the collapsed bag is then collected. The bag is then quickly filled with a known volume (60 liter at 10 liter/min.) of air which is free of all hydrocarbons and has a controlled level of CO_2. After the bag is partially inflated, an "emission rate" sample is collected, while zero air continues to flow into the enclosure at a rate slightly higher than the sample rate (approximately 2 liter/min.). The total enclosure time is approximately 15 minutes. The emission rate is equal to the difference in the hydrocarbon content of the bag measured in the emission rate sample minus the hydrocarbon content of the bag as measured in the background sample collected prior to inflation with zero air. This emission rate is then divided by some unit of foliage such as by leaf biomass. The result is a raw emission rate of the units: micrograms emission per gram leaf biomass per hour (µg/g/hr).[9]

This method has been used by Zimmerman to measure hydrocarbon emission rates for various biogenic sources in the Tampa, Florida,[10] and Houston, Texas,[11] areas.

To compare the enclosure method to the flux method, enclosure method measurements were made on loblolly pine at the IBP site from February through August 1977. Thirty-one determinations were made on both mature trees and saplings. The basic method used was the same as Zimmerman's,

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although the specific procedures were slightly different, and most of the samples were collected in Tedlar bags rather than in SS cans.

THEORY

The limb of a tree is enclosed in a large flexible plastic bag, and the bag opening is secured around the limb with tape, between the trunk and the leaves. After the bag is partially evacuated, a "background" sample is collected. The "dead volume" of the bag is estimated at the midpoint of the background sample. A known volume of clean air is then added to the bag at a constant rate over a known period of time. At the end of this time period an "emission sample" is collected. After the sampling has been completed, the limb is clipped, dried, and the leaves weighed.

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The mass of gaseous natural hydrocarbon in the enclosure bag increases over time, and if the emission rate is assumed to be constant over the short measurement period, then the plot of mass versus time is a straight line. The background sample period is t_1-t_0, the clean air addition period is t_3-t_2, and the emission sample period is t_5-t_4. Under normal field conditions, $t_1=t_2$ and $t_3=t_4$. The emission rate, dm/dt, is the slope of the mass versus time plot and is determined from the coordinates of two points along the plot. Therefore,

$$\frac{dm}{dt} = \frac{m_2-m_1}{(t_4 + t_5)/2 - (t_0 + t_1)/2} \qquad \text{(Eq.13)}$$

The masses, m_1 and m_2, are determined by measuring the hydrocarbon concentrations and enclosure bag volumes at the times $(t_0 + t_1)/2$ and $(t_4 + t_5)/2$. The hydrocarbon concentrations of the samples collected during the two time periods are the mean concentrations and correspond to the midpoints of the two time periods.

$$m_1 = V_d \cdot [HC]_b \qquad \text{(Eq.14)}$$

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where $[HC]_b$ is the concentration of the background sample and V_d, the dead volume, is the volume of the enclosure bag at time $(t_0 + t_1)/2$, and estimated visually.

$$m_2 = V_e \quad [HC]_e \qquad \text{(Eq.15)}$$

where $[HC]_e$ is the concentration of the emission sample and V_e is the volume of the enclosure bag at time $(t_4 + t_5)/2$ V_e can be determined by

$$V_e = V_d + V_a - 1/2\ V_s \qquad \text{(Eq.16)}$$

where V_d is the dead volume, V_a is the volume of clean air added, and V_s is the volume of emission sample removed.

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$$V_a = Q_a\ (t_3-t_2) \quad \text{and} \qquad \text{(Eq.17)}$$

$$V_s = Q_s\ (t_5-t_4) \qquad \text{(Eq.18)}$$

where Q_a is the clean air flow rate and Q_s is the sample flow rate. Substituting Equations 5 and 6 into 4 yields

$$V_e = V_d + Q_a\ (t_3-t_2) - 1/2\ Q_s\ (t_5-t_4) \qquad \text{(Eq.19)}$$

and substituting Equations 2 and 7 into 1 yields

$$\frac{dm}{dt} = \frac{(V_d + Q_a\ (t_3-t_2) - 1/2\ Q_s(t_5-t_4)) \cdot [HC]_e - (V_d \cdot [HC]_b)}{(t_4 + t_5)/2 - (t_0 + t_1)/2} \qquad \text{(Eq.20)}$$

The emission rate per unit of dry needle biomass is

$$ER = (dm/dt)/M \qquad \text{(Eq.21)}$$

where M is the dry needle mass. Thus,

$$ER = \frac{(V_d + Q_a\ (t_3-t_2) - 1/2\ Q_s\ (t_5-t_4)) \cdot [HC]_e - (V_d \cdot [HC]_b)}{M((t_4 + t_5)/2 - (t_0 + t_1)/2)} \qquad \text{(Eq.22)}$$

Equation 22 was the working equation for the emission rate determinations. A summary of the units employed is as follows: ER, µg/g/min; $[HC]_e$ and $[HC]_b$, g/L; V_d, L; Q_a and Q_s, L/min; time, min; and M, g.

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EXPERIMENTAL

The system and equipment used for enclosure method measurements at the IBP site are diagrammed in Figure 7. The enclosure bag was made of 2-mil-thick Teflon FEP film with dimensions of 1.0 m x 1.2 m and a volume of 200 L. A Thomas (Thomas Industries, Inc., Sheboygan, Wisconsin) Teflon TFE diaphram pump energized by a 12-volt battery was used to evacuate the bag and collect the samples. The pump's flow rate was 10 L/min. The clean air was Scott (Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania) zero air (THC less than 1.0 ppm and ambient carbon dioxide concentration), and the Teflon lines were all 0.25-inch (0.64 cm) o.d. FEP Teflon.

The measurement procedure was as follows: (a) Enclosed limb with Teflon bag with lines and thermometer in place. Taped bag around limb. (b) Withdrew air from bag down to a volume of 10 to 15 L. (c) Collected one minute background sample in Tedlar bag. Estimated dead volume; recorded t_0 and t_1. (d) Added clean air to enclosure bag at rate of 10 L/min for 5 min. Recorded temperature and times t_2 and t_3. (e) Collected one minute emission sample in Tedlar bag; recorded t_4 and t_5. (f) Removed enclosure bag and lines. (g) Cut the branch at tape point; dried for 2 days at 70°C; weighed needles. (h) Analyzed background and emission samples by GC. (i) Measured GC peaks and calculated concentrations. (J) Calculated emission rate.

The differences between this procedure and Zimmerman's were that Tedlar bags rather than stainless steel cans were used to collect the GC samples, and Zimmerman continued zero air flow at 2 L/min when collecting the emission rate sample, while no zero air was put into the bag during EPA sample collection.

The same GC system and columns that were used for the α-pinene flux determinations were also used for the enclosure method analyses. A typical chromatogram of an enclosure method sample is shown in Figure 8.

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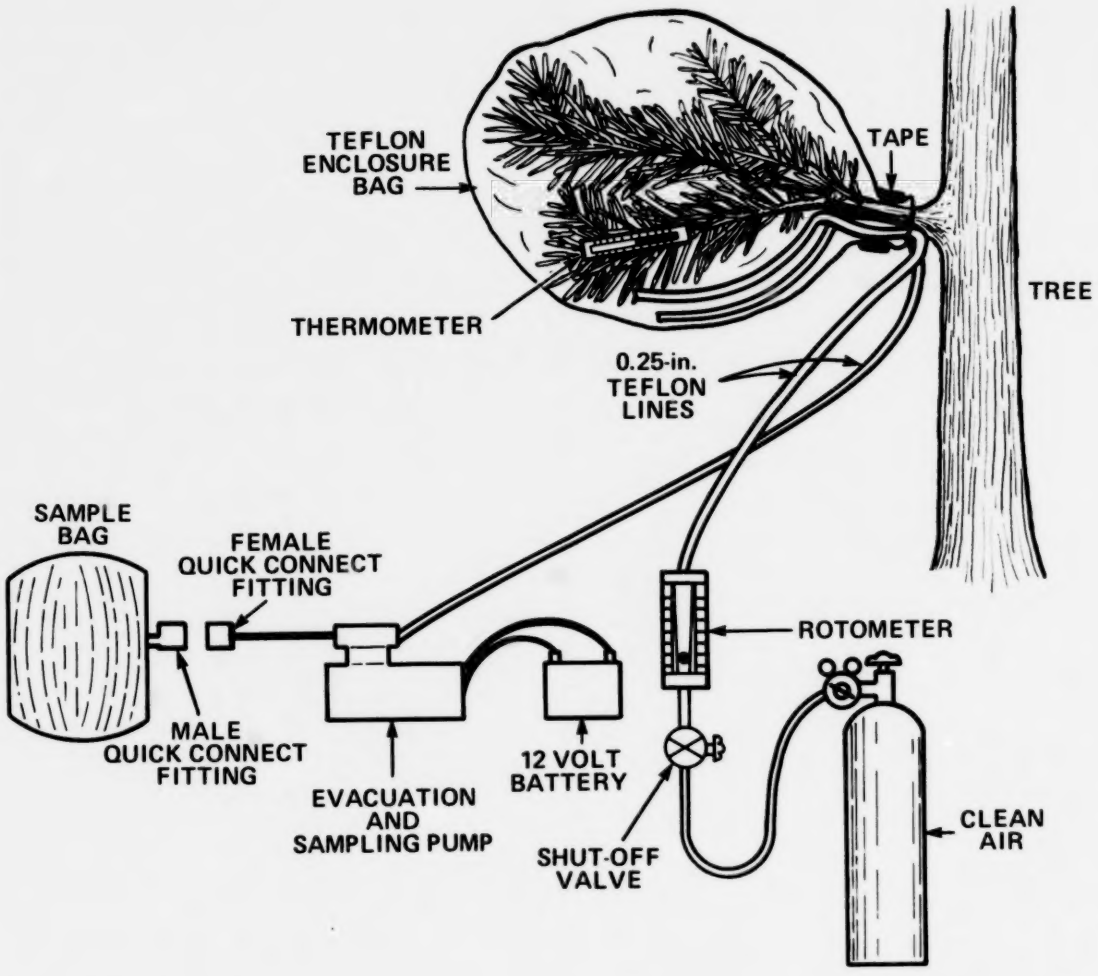

Figure 7. Enclosure method sampling system.

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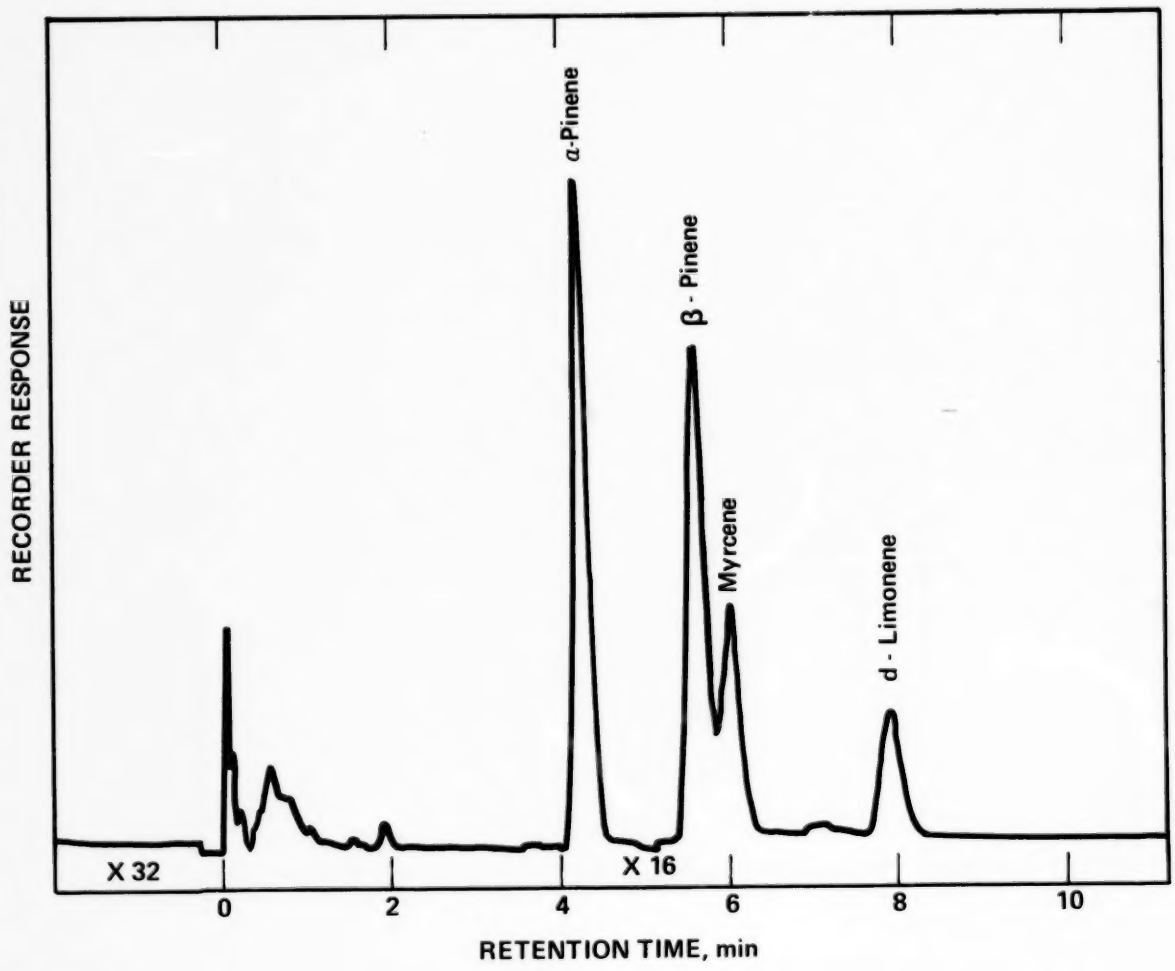

Figure 8. Enclosure method chromatogram.

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RESULTS

Emission rate measurements of α-pinene, β-pinene, myrcene, and d-limonene from loblolly pine were made at the Saxapahaw IBP site using the enclosure method previously described. Measurements were made from February through August 1977. The results of these measurements are reported in Table 3. Fifteen separate trees, indicated by the column labeled "tree identifier"--five of which were saplings--were used for measurements. Repeat determinations were made on five of the trees to determine the repeatability of the enclosure method. The numbers in parentheses after the tree identifier identify the repeated measurements which were performed on 4 different trees and 1 sapling. It should also be noted that 3 of the measurements yielded negative emission rates, the reason for which will be discussed later.

TABLE 3. SUMMARY OF LOBLOLLY PINE TERPENE EMISSION RATES* DETERMINED BY ENCLOSURE METHOD

Date	α-Pinene	β-Pinene	Myrcene	d-Limonene	Total	Temperature in Bag, °C	Tree Identifier†
			Eighteen-year-old trees				
2/25	4.80	2.47	0.39	0.28	7.94	19	1
2/25	8.09	3.43	1.21	0.35	13.08	26	2
3/03	11.25	4.10	1.77	0.49	17.61	16	3
3/03	3.49	1.45	0.20	0.18	5.32	17	4
7/21	31.86	5.38	1.31	7.73	46.28	43	5
8/02	2.27	0.90	0.82	0.42	4.41	32	6
8/02	3.27	1.15	0.25	0.22	4.89	32	7(1)
8/02	4.70	1.44	0.51	0.38	7.03	32	7(1)
8/08	20.88	6.14	1.01	0.90	28.93	37	8(2)
8/08	3.25	0.58	-0.30	-0.39	3.83	37	8(2)
8/08	5.81	1.71	0.37	0.24	8.13	38	8(3)
8/12	1.90	0.88	0.52	0.20	3.50	39	8(3)
8/08	1.23	0.94	0.43	0.19	2.79	35	9(4)
8/08	1.92	1.70	0.13	0.05	3.80	35	9(4)
8/12	1.72	1.25	0.78	0.64	4.39	38	9
8/12	9.10	9.48	2.54	0.90	22.02	42	10(5)
8/12	7.81	9.61	2.45	0.71	20.58	43	10(5)
			Saplings				
2/25	1.86	0.99	0.56	0.42	3.83	19	11
6/07	54.27	19.29	13.38	15.25	102.29	22	12
6/08	12.65	4.97	2.07	2.98	22.67	25	12
6/08	19.00	6.13	0.80	1.70	27.63	31	13
7/18	24.82	3.44	9.22	2.26	39.74	44	14
7/19	11.38	2.19	1.43	0.72	15.72	39	14
8/01	96.66	14.69	1.59	0.87	113.81	37	15(6)
8/01	65.04	12.01	0.88	1.01	78.94	37	15(6)
8/01	45.91	-4.68	1.60	0.79	48.30	37	15(6)

*Emission rate units are µg/g/h
†Numbers in parentheses identify the repeat samples.

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SECTION 5

DISCUSSION

ENERGY BALANCE/BOWEN RATIO METHOD

Error Analysis

Since terpenes are highly reactive with ozone, estimates were made to determine the effect of ambient ozone concentrations on the α-pinene gradient above the canopy. If we assume a steady state concentration of ozone of 0.08 ppm, the dilution and reaction can be viewed as competing first order processes. Hence, a pseudo-first order rate constant $k_{ozone} = 2.88 \times 10^{-4}$ s^{-1} is calculated using Grimsrud's rate constant of 3.6×10^{-3} ppm^{-1} s^{-1} [25]. To calculate the observed first order rate constant which includes both dilution and reaction, we substituted measured α-pinene concentrations of a typical profile (Figure 6). The estimated maximum (worst case) time required for an α-pinene molecule to rise from the lowest sampling point (16.5 m) to the highest point (27 m) above the canopy is 30 s. Hence, $(k_{dil} + K_{ozone})$ is equal to $[\ln(\alpha\text{-pinene})_{16.5m} - \ln(\alpha\text{-pinene})_{23m}] \div 30$ s. In the case of Figure 6 this is 0.018 s^{-1}. Therefore, we see that the effect of reaction on the α-pinene gradient is small (2%) within the range of measurement. The steady state assumption for ozone was supported by actual field measurements. No significant ozone gradient could be detected in the 6.5 m zone above the canopy.

Linear regressions, based on two sets of six pairs of observations for each measurement period, were used to define the Bowen (Eq. 10) and the α-pinene/water vapor density (Eq. 12) ratios and to estimate their accuracy. As for the observations used to define the ratio, the absolute precision of the air and dew point temperatures were ±0.01°C, and the relative accuracy of the α-pinene concentrations was ±10%. Based on an analysis technique for propagation of measurement errors [26] and estimates of the errors in the linear regression, the relative standard errors for the

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regression estimates of the Bowen and α-pinene/water vapor density ratios were ±5% and ±15% respectively.

When these ratios were used in conjunction with the net radiation observations (relative accuracy 2.5%), the relative standard errors of the latent heat and α-pinene flux calculations were ±5% and ±17%, respectively. The magnitude of the resultant relative error depended on the magnitude of the gradients of individual variables. Smaller relative errors were associated with larger gradients. In most cases, the predominant fraction of the error was due to the α-pinene data.

Neglecting the soil heat flux, G, and storage, S, terms in the energy balance would have resulted in overestimating the α-pinene flux by about 7% during the time of day when the data were collected. The photosynthesis flux was used in the energy balance calculations, although it had little effect on the estimate of the α-pinene flux.

Results and Correlations

Most of the data were collected during an abnormally hot and dry summer when temperatures ranged between 28-35°C (Table 2). For the temperature range 28 to 34°C, α-pinene fluxes ranged from 19 to 84 $\mu g/m^2/min$ with a mean of 43 $\mu g/m^2/min$.

The total α-pinene emission from a forest is a summation of the emission from all living and dead vegetative surfaces (foliage, bark, and litter). For each of the component surfaces, the α-pinene emission depends on the amount of surface, density of resin ducts, pathway for diffusion of the vaporized compounds, and temperature (i.e. vapor pressure) at the vaporizing surface. Only partial information about these characteristics of the emitting surfaces were available for this study. A previous study at this research site[22,27] provided predictive equations for estimating the total bark surface and the seasonal changes in foliage surface. In April, the foliar density was at its seasonal minimum and by August, the foliar density had increased by 40-50%. Stomatal diffusion measurements by Gresham[28] indicated very little daytime or seasonal change in the foliage pathway diffusion resistances except under conditions of extreme drought. Air temperature measurements concurrent with the α-pinene flux measurements provided an

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approximate estimate of the surface temperature (vapor pressure). Concurrent measurements of water evaporation and net carbon dioxide exchange provided information about physiological parameters that could be related to the α-pinene emission. However, no information was available about either the effective litter surface or the density of resin ducts for any of the surfaces.

Simple correlations were used to relate these initial estimates of the flux of α-pinene from loblolly pine to the available vegetation and environmental parameters. None of these correlations were significant. No obvious trends were found between emission increases and increasing temperature, foliage surface area, water evaporation, or net carbon dioxide exchange. Rasmussen[8] observed an increase in α-pinene emission as the temperature of foliage (placed in a bell jar) was increased. In our studies, the lowest emissions occurred at the lowest temperatures (7 April); however, the limited amount of low temperature data (two observations) was not adequate to indicate a significant difference from the higher temperature data as shown in Figure 9.

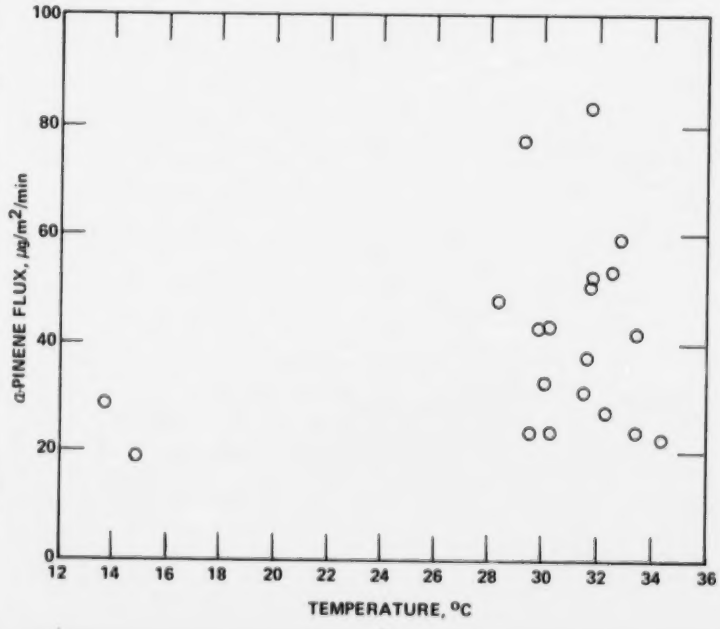

Figure 9. α-pinene flux vs. ambient temperature.

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ENCLOSURE METHOD

Error Analysis

The variance of the enclosure method has two components: the natural variation inherent in the emission itself due to environmental effects and the error of the analytical method. The error of the method itself which includes sampling and analysis errors was estimated to be ±20%, by propagation of estimated errors of the input variables of Equation 22. To determine the actual variance of the method, six repeat determinations were performed: duplicate determinations on four separate limbs and a triplicate determination on one sapling. The repeat determinations were made by adding more zero air to the enclosure bag and sampling a third or fourth time. The repeatability data for α-pinene is presented in Table 4. The relative standard deviations varied widely from 11% to 103% with a mean of 47%. Of note, also, is that for four of the six repeat determinations, the later values were smaller than the earlier values. This suggests a possible bias in the analytical method. This apparent bias could be due to the physical contact between enclosure bag and limb causing higher initial emissions in the bag. Great care must be exercised when using this method not to damage the vegetation with the enclosure bag, for it is well known that such damage would indeed cause higher emissions. The difference between the ±20% estimated analytical error and ±47% measured standard deviation is probably due to the bias previously mentioned, along with actual vegetative variability. Natural variance between different trees of the same species and limbs of the same tree would be expected, as well as variance attributed to environmental factors such as temperature, humidity, soil nutrient, and moisture conditions. The relatively high variance of the method along with possibly poor dead volume estimates may account for the negative emission rates in Table 3.

Both saplings and limbs from mature trees were used for enclosure method determinations. Table 5 shows that the results from saplings were very much higher than those from the mature trees. The skewness of the two data sets as evidenced by means considerably higher than medians,

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and the relatively high standard deviations also suggest the previously mentioned effect of increased emissions due to physical contact between enclosure bag and vegetation. It may be that the saplings were more easily distrubed by this method of sampling than the mature limbs.

TABLE 4. ENCLOSURE METHOD REPEATABILITY DATA

α-Pinene emission rates (μg/g/h)			Mean	Standard deviation	Relative Standard deviation (%)
3.27	4.70		3.99	1.01	25
20.88	3.25		12.07	12.47	103
5.81	1.90		3.86	2.76	72
1.23	1.92		1.58	0.49	31
9.10	7.81		8.46	0.91	11
96.66	65.04	45.91	69.20	25.63	37

TABLE 5. COMPARISON OF LOBLOLLY PINE SAPLING AND MATURE TREE α-PINENE EMISSION RATES DETERMINED BY THE ENCLOSURE METHOD

Type of Tree	No. of Points	Median (μg/g/h)	Mean (μg/g/h)	Standard Deviation
Saplings	9	24.8	36.8	31.0
Mature trees	17	4.7	7.3	8.0

COMPARISON OF METHODS

A comparison of the enclosure method with the energy balance/Bowen ratio method is best accomplished by graphical means. This is because the emission rates were not all obtained at the same time or temperature, and the data is very scattered. Figure 10 shows this graphical comparison by a plot of log α-pinene emission rate versus temperature for the two data sets. The enclosure method data set includes only the measurements from mature trees. The regression line with 95% confidence bounds derived by Tingey et al.[14] for the α-pinene emission rate of slash pine is also included for reference and comparison. The graph suggests three things: (a) The two data sets are very scattered and indistinguishable

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from one another, (b) the enclosure method points show greater dispersion than the energy balance/Bowen ratio points, and (c) neither set of data show a log linear relation to temperature as Tingey found.

Since the data showed no perceptable temperature effect, a comparison of means statistical test (t-test) was performed.[29] The medians of the two data sets were used as the measures of central tendency rather than means, because the mean of the enclosure data set being much higher than the median suggested bias and the median is more accurate for small data sets where bias may be present.[30] The difference between the medians was not significant (α=0.25). Thus both the graph and the statistical comparison suggest that an hypothesis that one method yields higher (or lower) results than the other cannot be accepted. The data base is too small and variances too large for such a conclusion.

That the enclosure method has a higher variance than the energy balance/Bowen ratio method is supported by the wide difference between the calculated variances of the two data sets--3.04 versus 63.8. However both methods have relatively high variance and Tingey's 95% confidence bounds suggest a large dispersion in his results also.

Although we observed no log-linear relationship of α-pinene emission rate with temperature as Tingey did, it is interesting that Tingey's regression line seems to split both data sets rather evenly. For the energy balance/Bowen ratio method, 11 points are above the line and 9 below, and for the enclosure method, 10 points are above the line and 7 below. Tingey's α-pinene emission rate at 32^{o}C (mean temperature of the two data sets) is 3.65 µg/g/h, while the median enclosure method value was 4.70 µg/g/h and the median energy balance/Bowen ratio value was 3.58 µg/g/h. This comparison may not mean much, because we are comparing slash pine seedlings with mature loblolly pine trees, but it does suggest that all of the numbers are in the same range. The lack of visible log-linear relationship between emission rate and temperature for the enclosure method is probably due to the many environmental factors which cannot be controlled during field measurements but can be controlled to a much greater degree under laboratory conditions as Tingey did. The similar

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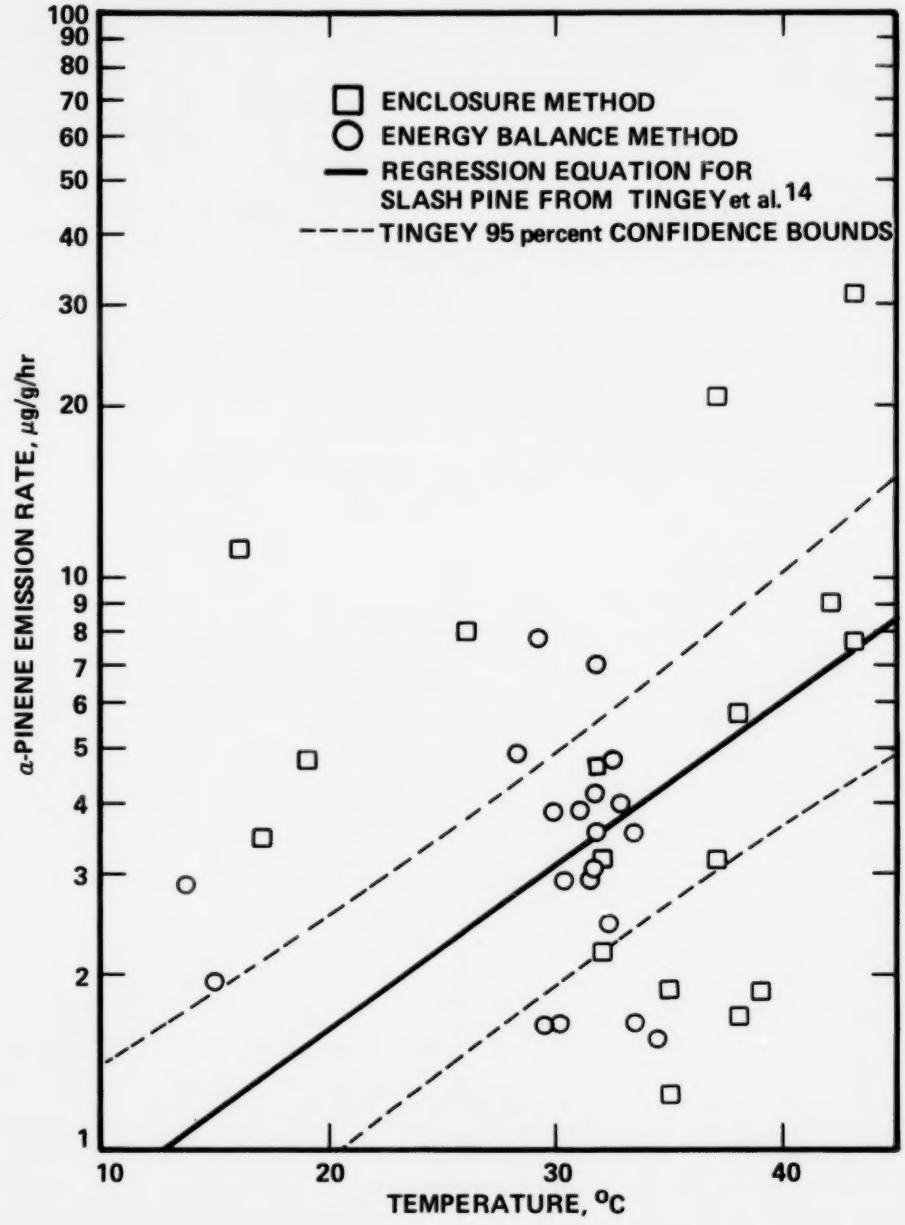

Figure 10. Comparison of α-pinene emission rates for loblolly pine by energy balance/Bowen ratio and enclosure methods.

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lack of a log-linear relationship for the energy balance/Bowen ratio results is due to lack of measurements over a wide enough temperature range to evaluate a temperature effect.

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REFERENCES

1. Ripperton, L. A., J. J. B. Worth, F. M. Vukovich, and C. E. Decker Research Triangle Institute Studies of High Ozone Concentrations in Nonurban Areas. International Conference on Photochemical Oxidant Pollution and Its Control. EPA-600/3-77-001a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977. pp. 413-424.

2. Dimitriades, B., and A. P. Altshuller. International Conference on Oxidant Problems: Analysis of the Evidence/Viewpoints Presented. Part I. Definition of Key Issues. J. Air Poll. Control Assoc., 27 (4): 299-307, 1977.

3. Robinson, E., F. Vukovich, and D. H. Pack. International Conference on Oxidants, 1976-Analysis of Evidence and Viewpoints. Part V. The Issue of Oxidant Transport. EPA-600/3-77-117, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977. 70 pp.

4. Singh, H. B., W. Viezee, W. B. Johnson and F. L. Ludwig. The Impact of Stratospheric Ozone on Tropospheric Air Quality. J. Air Poll. Control Assoc., 30(9): 1009-1017, 1980.

5. Coffey, P. E., and H. Westberg. International Conference on Oxidants, 1976-Analysis of Evidence and Viewpoints. Part IV. The Issue of Natural Organic Emissions. EPA 600/3-77-116, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977. 51 pp.

6. Arnts, R. R. and B. W. Gay, Jr. Photochemistry of Some Naturally Emitted Hydrocarbons. EPA-600/3-79-081, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1979. 128 pp.

7. Went, F. W. Organic Matter in the Atmosphere, and Its Possible Relation to Petroleum Formation. Proc. Nat. Acad. Sci., 46(2): 212-221, 1960.

8. Rasmussen, R. A. What Do the Hydrocarbons from Trees Contribute to Air Pollution? J. Air Poll. Control Assoc., 22(7): 537-543, 1972.

9. Zimmerman, P. R. Testing of Hydrocarbon Emissions from Vegetation, Leaf Litter and Aquatic Surfaces, and Development of a Methodology for Compiling Biogenic Emission Inventories. EPA-450/4-79-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1979. 103 pp.

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10. Zimmerman, P. R. Determination of Emission Rates of Hydrocarbons from Indigenous Species of Vegetation in the Tampa/St. Petersburg, Florida, Area. EPA-904/9-77-028. U.S. Environmental Protection Agency, Atlanta, Georgia, 1979, 161 pp.

11. Zimmerman, P. R. Natural Sources of Ozone in Houston: Natural Organics. In: Proceedings of the APCA Speciality Conference II on Ozone/Oxidant Interaction with the Total Environment, E. R. Frederick, ed., Houston, Texas. 1979. pp. 299-310.

12. Flyckt, D. L. Seasonal Variation in the Volatile Hydrocarbon Emissions from Ponderosa Pine and Red Oak. M.S. Thesis, Washington State University, Pullman, Washington, 1979, 53 pp.

13. Tingey, D. T., M. Manning, L. C. Grothaus, and W. F. Burns. The Influence of Light and Temperature on Isoprene Emission Rates from Live Oak. Physiol. Plant., 47:112-118, 1979.

14. Tingey, D. T., M. Manning, L. C. Grothaus, and W. F. Burns. Influence of Light and Temperature on Monoterpene Emission Rates from Slash Pine. Plant Physiol., 65:797-801, 1980.

15. Gay, L. W., and K. R. Knoerr. The Forest Radiation Budget. Bulletin No. 19, School of Forestry and Environmental Studies, Duke University, Durham, North Carolina, 1975. 165 pp.

16. Parmele, L. H., E. R. Lemon, and A. W. Taylor. Micrometeorological Measurements of Pesticide Vapor Flux from Bare Soil and Corn Under Field Conditions. Air, Water, and Soil Pollution, 1: 433-451, 1972.

17. Knoerr, K. R. Contrasts in Energy Balances Between Individual Leaves and Vegetated Surfaces. In: International Symposium of Forest Hydrology. W. E. Sopper and H. W. Lull, ed., Pergamon Press, New York, 1966, pp. 391-401.

18. Geiger, R. The Climate Near the Ground. Harvard University Press, Cambridge, Massachusetts, 1965. 611 pp.

19. Stewart, J. B. and A. S. Thom. Energy Budgets in Pine Forest. Q. J. R. Meteor. Soc. 99:154-170, 1973.

20. Burgess, R. L. and R. V. O'Neill, eds. Eastern Deciduous Forest Biome, Progress Report, Report EDFB-IBP 75-11, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1974, pp. 63-71.

21. Buzzard, G. H., T. R. Sinclair and K. R. Knoerr. Measurement of Atmospheric Water Vapor and CO_2 Profiles for Evaluation of the Turbulent Transfer Processes of a Loblolly Pine Forest. Memo Report #72-74, International Biological Program, Eastern Deciduous Forest Biome, Triangle Research Site, U.S. Atomic Energy Commission, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1972. 24 pp.

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22. Sinclair, T. R. , G. H. Buzzard and K. R. Knoerr. A Pressure Method for Frequent Differential Calibration of CO_2 Infrared Analyzer. Photosynthetica, 10(2):188-192, 1976.

23. Seila, R. L. Non-Urban Hydrocarbon Concentrations in Ambient Air North of Houston, Texas. EPA-600/3-79-010, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1979. 30 pp.

24. Kinerson, R. S., K. O. Higginbotham, and R. C. Chapman. The Dynamics of Foliage Distribution within a Forest Canopy. J. Appl. Ecol., 11: 347-353, 1974.

25. Grimsrud, E. P., H. H. Westberg, and R. A. Rasmussen. Atmospheric Reactivity of Monoterpene Hydrocarbons, NO_x, Photooxidation, and Ozonolysis. Int. J. of Chemical Kinetics, VII (supplement), Symposium No. 1, Chemical Kinetics Data for the Upper and Lower Atmosphere, S. W. Benson, ed. John Wiley and Sons, New York, 1975. pp. 183-195.

26. Topping, J. Errors of Observation and Their Treatment. Reinhold Publishing Corp., New York, 1957. 119 pp.

27. Ralson, C. W. Annual Primary Productivity in a Loblolly Pine Plantation. In: Inter. U. Forest Res. Org. Biomass Studies, H. E. Young, ed., University of Maine, Orono, Maine, 1974, pp. 105-117.

28. Gresham, C. Stomatal Resistance in a Loblolly Pine Planatation. Ph.D. Thesis, Duke University, Durham, North Carolina, 1975, 176 pp.

29. Bennett, C. A. and N. L. Franklin. Statistical Analysis in Chemistry and the Chemical Industry. John Wiley and Sons, Inc., New York, 1954. pp. 176-180.

30. Dean, R. B. and W. J. Dixon. Simplified Statistics for Small Numbers of Observations. Anal. Chem., 23(4):636-638, 1951.

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